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## PATENT SPECIFICATION

Convention Date (Germany) : Oct. 17, 1932.

420,052



Application Date (in United Kingdom) : Oct. 16, 1933 No. 17,056 / 34.

(Divided out of Application No. 28,530/33.)

(Patent of Addition to No. 386,161 : dated March 10, 1931 and to No. 386,161 as improved upon or modified by No. 393,505 : dated March 9, 1932.)

Complete Specification Accepted : Nov. 23, 1934.

## COMPLETE SPECIFICATION.

## Manufacture of Shaped Articles from Polyvinyl Alcohols.

We, CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE G.M.B.H., a Body Corporate organised according to the laws of Germany, of 20, Zielstattstrasse, Munich, Germany, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

10 This invention is an improvement in or modification of that described in Specification No. 386,161. In that specification and in Specification No. 393,505 it has been shown that threads, cords, 15 ribbons, tubes and the like made from polyvinyl alcohol are distinguished by the property that they can be tolerated by the body without reaction and, in particular, that when used for surgical sutures they do 20 not cause suppuration or give rise to the formation of fistulae.

Although ability to be resorbed is not desired or necessary in all cases, for instance in a substitute for silk for 25 surgical purposes, it is nevertheless of great importance that one should be in a position to impart by suitable additions to polyvinyl alcohols which are resorbed not at all or only insufficiently a capacity 30 for being resorbed which can be graded as desired by suitable selection of the magnitude of the addition. In Specifications Nos. 386,161 (as open to inspection under Section 91 of the Acts) and 35 303,505 we have shown that the result can be attained by an addition of, among other substances, borax.

The possibility of increasing by suitable additions the capacity for being 40 resorbed of polyvinyl alcohols which are resorbed with difficulty, already expressed in Specification No. 393,505, is considerably extended in its application by the present invention. It has now been found that 45 additions of electrolytes other than borax are effective in increasing the capacity for being resorbed. Among the large number of additions which come into question

some will now be mentioned. For example, organic acids such as oxalic acid, 50 malic acid or lactic acid are active, and especially those acids which are substituted by negative or positive radicals. Thus sulpho-salicylic acid, benzene-sulphonic acid, toluene-sulphonic acid, tri- 55 chloroacetic acid, glycol and asparaginic acid are very active. Phenyl-hydrazine hydrochloride is also very active. Inorganic electrolytes (other than borax) such as nickel nitrate, potassium bi- 60 chromate and others also improve the capacity for being resorbed.

Modifications of polyvinyl alcohol which are not resorbed or are resorbed insufficiently can be rendered more easily 65 resorbable by the incorporation of para-toluene sulphonic acid, benzene-sulphonic acid, sulpho-salicylic acid, trichloroacetic acid or phenyl-hydrazine hydrochloride. In general an addition amounting to a few per cents. for example 5—10 per cent, is sufficient. The capacity for being 70 resorbed can be graded as required by the magnitude of the addition. If the capacity for being resorbed is too great, the quantity of the addition is diminished and vice versa. The substances which 75 promote resorption, as well as the further additions hereinafter to be referred to, can be added under suitable circumstances to the parent material, serving for the production of the polyvinyl alcohol. For 80 example, if threads of polyvinyl alcohol are to be made by spinning a solution of an ester or acetal and subsequently saponifying the threads thus obtained, the additional substances may if required be incorporated in the solution which is to be spun.

In case of necessity the strength of the threads and the like from polyvinyl alcohol can also be suitably increased. This object may be attained, for 90 example, by the addition of suitable electrolytes, among which there may be named particularly sulphocyno com- 95

pounds, such as potassium sulphocyanide or ammonium sulphocyanide. An addition of borax or of a sugar, such as cane sugar, also produces a very considerable increase in strength. In this case also additions of about 5—10 per cent, suffice, but obviously the quantity can be varied according to requirements and to the desired result.

There also comes into consideration the addition of substances having a bactericidal action. Any bactericidal substance which is compatible with the polyvinyl alcohol is suitable. From the large number of bactericidal substances of various groups there may be mentioned by way of example esters of aromatic acids, such as propyl benzoate, also salts, compounds or sols of metals such as silver, mercury, bismuth, arsenic and others. Sulphur compounds and other substances having a bactericidal action also come into consideration.

For example, threads of polyvinyl alcohol acquire strong bactericidal properties when there is incorporated in them propyl benzoate or mercuric chloride. Even small quantities of these additions generally suffice, depending on their bactericidal action.

The formed articles in accordance with the invention are mainly of importance in the sphere of surgery. However, the possibility of producing them with a desired capacity for being resorbed and with desired therapeutically active additions also renders them useful, in the form of capsules, pills, plugs and the like, for other medicinal purposes. The products are of course also applicable in other spheres. For example, threads of this kind come into question in the production of hygrometers; fabrics made from the threads are useful for the production of special clothing, and so on. Depending on the purpose for which the products are to be used, the addition of a hydrophobe substance, a softening agent, a filler, a dyestuff or the like may be of advantage.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to

be performed, we declare that what we claim is:—

1. Threads, cords, ribbons, tubes and the like applicable especially for medicinal purposes and principally for sutures in surgery, for example, as substitutes for catgut, silk, twine, horse-hair and the like, consisting of a polyvinyl alcohol or a mixture or combination of different polyvinyl alcohols with another or with other substances, containing as an addition which promotes resorption at least one organic or inorganic electrolyte other than borax, especially oxalic acid, malic acid, lactic acid and acids which are substituted by negative or positive radicals, phenyl hydrazine hydrochloride, nickel nitrate and salts working in a similar manner.

2. Threads, cords, ribbons, tubes and the like as defined in Claim 1, containing an aromatic sulphonic acid.

3. Threads, cords, ribbons, tubes and the like as defined in Claim 1 or Claim 2, containing a substance which increases their strength, substantially as described.

4. Threads, cords, ribbons, tubes and the like as defined in Claim 1, 2 or 3, containing a substance having a bactericidal or therapeutic action.

5. Plugs, pills, capsules and the like consisting of a polyvinyl alcohol or a mixture or combination of different polyvinyl alcohols with one another or with other substances, containing as an addition which promotes resorption at least one organic or inorganic electrolyte other than borax, especially oxalic acid, malic acid, lactic acid and acids which are substituted by negative or positive radicals, phenyl hydrazine hydrochloride, nickel nitrate and salts working in a similar manner, and containing or enclosing a therapeutically active substance.

6. Plugs, pills, capsules and the like as defined in Claim 5, containing a substance referred to in Claim 2, 3 or 4.

Dated this 8th day of June, 1934.

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